

# PATENT ABSTRACTS OF JAPAN

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## **(54) POLYMER COMPOSITE**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To develop a composite material having excellent dispersibility of a carbon nanotube therein, which is useful as a semiconductor material and a conducting material as a substitute of conventional inorganic materials.

**SOLUTION:** The polymer composite comprises a mono- or multi-layered carbon nanotube and a straight chain conjugate polymer.

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## CLAIMS

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[Claim(s)]

[Claim 1] The polymer composite which consists of a monolayer carbon nanotube or a multilayer carbon nanotube, and a straight chain-like conjugated-system polymer.

[Claim 2] The polymer composite according to claim 1 whose straight chain-like conjugated-system polymer is the poly thiophene system polymer.

[Claim 3] The polymer composite according to claim 2 whose poly thiophene system polymers are a Polly 3-alkyl thiophene and/or a Polly 3-alkoxy thiophene.

[Claim 4] The polymer composite according to claim 3 whose Polly 3-alkyl thiophene is a Polly 3-hexyl thiophene.

[Claim 5] A polymer composite given in any 1 term of claims 1-4 whose weight ratios of the monolayer carbon nanotube to a straight chain-like conjugated-system polymer or a multilayer carbon nanotube are 1 or less % of the weight 0.1 % of the weight or more.

[Claim 6] A polymer composite given in any 1 term of claims 1-4 which the weight ratio of the monolayer carbon nanotube to a straight chain-like conjugated-system polymer or a multilayer carbon nanotube exceeds 3 % of the weight, and are 900 or less % of the weight.

[Claim 7] A polymer composite given in any 1 term of claims 1-4 whose weight ratios of the monolayer carbon nanotube to a straight chain-like conjugated-system polymer or a multilayer carbon nanotube are 100 % of the weight or more and 900 % of the weight or less.

[Claim 8] The polymer composite according to claim 7 which is a film-like.

[Claim 9] The manufacture approach of the film-like polymer composite according to claim 8 characterized by carrying out the carbon nanotube which consisted of the straight chain-like conjugated-system polymer, a carbon nanotube, and a solvent, and the carbon nanotube distribution solution whose weight ratios of the carbon nanotube to a straight chain-like conjugated-system polymer are 3 % of the weight or more and 900 % of the weight or less to the straight chain-like conjugated-system polymer bound a \*\* exception.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to the polymer composite which consists of a carbon nanotube and a straight chain-like conjugated-system polymer.

#### [0002]

[Description of the Prior Art] Applied possibility is examined by the extensive field as a material with nanotechnology leading [ a carbon nanotube (henceforth CNT) ]. It is divided into the approach of using the single track of CNT like a transistor or the probe for microscopes as an application, and the approach of summarizing much CNT(s) like an electron emission electrode, the electrode for fuel cells, or the conductive composite that distributed CNT, and using it as bulk. Although it is indispensable that it can distribute good in the polymer which serves as a matrix material in a conductive composite etc., generally CNT has the problem of being hard to distribute. For this reason, the approach of improving dispersibility by reforming on the front face of CNT, chemical modification, etc. is taken.

#### [0003]

[Problem(s) to be Solved by the Invention] However, when the front face of CNT is reformed, there is a problem that the property of original CNT, for example, high conductivity, is spoiled. As an approach of making a polymer distributing CNT, the method of making a spiral polymer distribute CNT is learned, without reforming the front face of CNT. As such a polymer, Poly m-phenylenevinylene-co-dioctoxy-p-phenylenevinylene (patent reference 1 reference), a polyvinyl pyrrolidone (nonpatent literature 1 reference), and Poly-phenylacetylene are used, for example. However, since conjugated system will not be enough connected if spiral structure is generally taken, a motion of the charge within a polymer is late and there is a trouble of being inadequate for using conductivity and a semi-conductor property.

[0004] Then, that this invention should solve the above-mentioned trouble, it excels in the dispersibility of CNT and sets it as the purpose to offer the polymer composite which can control electric conductivity by concentration of CNT.

#### [0005]

[Patent reference 1] JP,2000-44216,A [0006]

[Nonpatent literature 1] Chemical Physics Letters 342 (2001) 265-271 The 267th page

#### [0007]

[Means for Solving the Problem] In order to attain the above-mentioned technical problem, this invention consists of the following configuration.

[0008] That is, this invention is a polymer composite which consists of a monolayer

carbon nanotube or a multilayer carbon nanotube, and a straight chain-like conjugated-system polymer.

[0009]

[Embodiment of the Invention] As a result of considering distribution of CNT to a polymer wholeheartedly that the polymer composite which consists of CNT and a polymer should be developed, even if this invention persons were polymers which do not take spiral structure, they found out that it could distribute good. Furthermore, the polymer used in this invention has the features of being advantageous to conjugated-system structure being developed and using conductivity and a semi-conductor property in order not to take spiral structure.

[0010] Generally, a conjugated-system macromolecule can control conductivity by doping from a semiconductor region to a metal field, and things are known. Doping is performed by adding to a conjugated-system macromolecule by making electronic receptiveness or an electron-donative organic compound into a dopant. However, generally the doped conjugated-system macromolecule lacks in stability to heat or humidity, and when exposed to an elevated temperature or high humidity, it has the trouble that electric conductivity decreases greatly. This is for a dopant to secede from a conjugated-system macromolecule mainly under such conditions. In the polymer composite which consists of CNT and the polymer of this invention, electric conductivity can be controlled by concentration of CNT, and there are the features that the stability over heat or humidity is also excellent.

[0011] Hereafter, this invention is explained in full detail. The polymer which constitutes a composite in this invention needs to be a straight chain-like conjugated-system polymer. The skeletal structure of a macromolecule does not take spiral structure in a stable state (condition that external force is not added), the shape of a straight chain means a straight stretch \*\*\*\*\* thing, and, as for a conjugated-system polymer, association of the carbon-carbon of a macromolecule frame means the polymer with which 1-fold association and double association stand in a row by turns here.

[0012] As such a conjugated-system polymer, the poly thiophene system polymer, a polypyrrrole system polymer, the poly aniline system polymer, a polyacetylene system polymer, a Polly p-phenylene system polymer, a Polly p-phenylenevinylene system polymer, etc. are mentioned. In order for these conjugated-system polymers to be straight chains-like, as for the poly thiophene system polymer and a polypyrrrole system polymer, a monomeric unit needs to be connected in the 2 or 5th place of a thiophene ring and a pyrrole ring, respectively. Moreover, with the Polly p-phenylene system polymer and the Polly p-phenylenevinylene system polymer, the macromolecule frame is connected in the para position of a phenylene group. In this invention, the poly thiophene system polymer is especially used preferably also in the above-mentioned polymer.

[0013] The poly thiophene system polymer has the structure to which the side chain was attached to the polymer with the frame of Polly p-thiophene structure. As an example, Polly 3-methylthiophene, a Polly 3-butyl thiophene, Polly 3-alkyl thiophenes, such as a Polly 3-hexyl thiophene, a Polly 3-octyl thiophene, and a Polly 3-DESHIRU thiophene (especially for a limit, the carbon number of an alkyl group is 1-12 preferably, although there is nothing), Polly 3-alkoxy thiophenes, such as a Polly 3-methoxy thiophene, a Polly 3-ethoxy thiophene, and a Polly 3-dodecyloxy thiophene (especially for a limit, the carbon number of an alkoxy group is 1-12 preferably, although there is nothing), Polly 3-

alkoxy-4-alkyl thiophenes (especially for a limit, the carbon number of an alkoxy group and an alkyl group is 1-12 preferably, although there is nothing), such as Polly 3-methoxy-4-methylthiophene and Polly 3-dodecyloxy-4-methylthiophene, are mentioned. One sort or two sorts or more can be used. Especially, a Polly 3-alkyl thiophene and a Polly 3-alkoxy thiophene are desirable, and a Polly 3-hexyl thiophene is desirable especially as the former. Moreover, the above-mentioned polymer does not necessarily need to be the amount of macromolecules, and may be oligomer which consists of straight chain-like conjugated system.

[0014] Although CNT is produced by the arc discharge method, the chemical-vapor-deposition method (it considers as a CVD method below), the laser ablation method, etc., CNT used for this invention may be obtained by which approach. Moreover, there are a monolayer carbon nanotube (henceforth SWCNT) around which the carbon film (GURAFFEN sheet) of one sheet was wound in the shape of a cylinder, and a multilayer carbon nanotube (henceforth MWCNT) with which two or more GURAFFEN sheets of two or more sheets were wound around concentric circular in CNT, in this invention, it is a simple substance about SWCNT and MWCNT, respectively, or both sides are used for coincidence. Especially SWCNT is preferably used at the point which raises the mobility of a polymer composite and raises a semi-conductor property.

[0015] Since fullerene, graphite, and amorphous carbon are generated by coincidence as a byproduct and catalyst metals, such as nickel, iron, cobalt, and an yttrium, also remain in case SWCNT and MWCNT are produced by the above-mentioned approach, it is necessary to refine these impurities. Moreover, although CNT is generally formed in the shape of a string, when it is the conductive low range or uses a composite as a semi-conductor, it is desirable to cut CNT, before using a staple fiber-like thing or a fibrous thing. Sonication is effective in purification of the above-mentioned impurity or the cut to a staple fiber with the acid treatment by the nitric acid, a sulfuric acid, etc., and it is still more desirable to use separation with a filter together, when raising purity.

Although especially the diameter of CNT used by this invention is not limited, 1nm or more 100nm or less is desirable, and is 50nm or less more preferably.

[0016] It is obtained in the configuration which carried out orientation to the substrate front face perpendicularly by forming catalyst metals, such as iron and cobalt, for example on a substrate, pyrolyzing a carbon compound at 700-900 degrees C with a CVD method on the front face, and carrying out vapor growth of the CNT as an approach of producing CNT in the shape of a staple fiber beforehand. Thus, the produced shape of a staple fiber CNT can be taken out by stripping off from a substrate etc. Moreover, the shape of a staple fiber CNT can make a catalyst metal able to support on a porous base material like porous silicon, and the oxide film on anode of an alumina, and can also grow up CNT into the front face with a CVD method. CNT of the shape of a staple fiber which used as the raw material a molecule like the iron phthalocyanine which contains a catalyst metal in intramolecular, and carried out orientation also by the approach of producing CNT on a substrate by performing a CVD method in the gas stream of an argon/hydrogen is producible. Furthermore, the shape of a staple fiber CNT which carried out orientation to the SiC single crystal front face with the epitaxial grown method can also be acquired.

[0017] In this invention, by mixing the thing which made the straight chain-like conjugated-system polymer distribute CNT in a suitable solvent, a composite solution can

be prepared and the polymer composite of this invention can be obtained from this composite solution.

[0018] As a solvent used here, straight chain-like conjugated-system polymers, such as a methanol, toluene, a xylene, and chloroform, can mention a meltable thing preferably. Thus, with an ultrasonic washing machine, after irradiating a supersonic wave preferably for about 20 hours for several hours, in the obtained solution, it will be left about one day, and the coating liquid for spinner spreading can be obtained in it.

[0019] The above-mentioned conjugated-system polymer not only distributes CNT good, but is equipped with the features of making it distribute, while solving CNT condensed [ especially ] in the shape of a bundle by SWCNT in the state of the solution. Generally it is desirable that are condensing SWCNT in the shape of a bundle in the condition of having been manufactured, and CNT is solved and distributed from this bundle condition in a composite. For this reason, it is used, after giving chemical modification by the approach of making a functional group add to SWCNT etc. and giving dispersibility, as seen also in Science magazine vol.282 and p95 (1998) when SWCNT is distributed.

However, since pi conjugated system which constitutes CNT will be easy to be destroyed if chemical modification is given to CNT, there is a trouble that the property of CNT original is spoiled. Distribution of CNT is possible even if it does not give such chemical modification especially in this invention.

[0020] Although especially the weight ratio of CNT contained in the polymer composite of this invention is not limited, when the molar fraction of CNT exceeds 3 % of the weight, for example to a straight chain-like conjugated-system polymer, conductivity can be raised by leaps and bounds. At 3 or less % of the weight, although the molar fraction of CNT cannot make conductivity increase greatly, it can give the conductivity of extent which misses electrostatic charge. The mobility of a charge when the weight ratio of CNT uses a polymer composite as a semi-conductor material 0.1% of the weight or more to a straight chain-like conjugated-system polymer especially as it is 1 or less % of the weight can be raised, and it can use as a high performance semi-conductor material, and is desirable. On the other hand, since the conductivity of a polymer composite can be raised by leaps and bounds if the weight ratio of CNT increases, it can use as a conductor ingredient. Especially the weight ratio of CNT can exceed 3 % of the weight, and it can treat as a conductor ingredient to 900 or less % of the weight of a case. Furthermore, when the weight ratios of CNT are 100 % of the weight or more and 900 % of the weight or less, a matrix serves as CNT and the conductor composite of a gestalt to which a polymer exists in the clearance between CNT(s) can be obtained. Since this composite can be fabricated in the shape of a film, a composite film can be obtained, and since it can balance highly, the reinforcement as a film, conductivity, and binding capacity can be used preferably.

[0021] As an approach of obtaining a film-like composite, it consists of a straight chain-like conjugated-system polymer, CNT, and a solvent, and can obtain from the CNT distribution solution whose weight ratios of CNT to a straight chain-like conjugated-system polymer are 3 % of the weight or more and 900 % of the weight or less by classifying CNT which the straight chain-like conjugated-system polymer bound, for example. Although a filter is used, a distributed solution is carried out a \*\* exception or there is a method of it evaporating or being air-dry and classifying a solvent from a distributed solution etc. among the judgment approaches, when especially a \*\* exception

is performed, the weight ratio of CNT to a straight chain-like conjugated-system polymer can obtain 100% of the weight or more of a composite film. In addition, the ratio of the CNT and the straight chain-like conjugated-system polymer in a composite film is computable from the ratio of the carbon by elemental analysis, hydrogen, nitrogen, and sulfur. Moreover, this ratio can change the compounding ratio of the straight chain-like conjugated-system polymer in CNT dispersion liquid, and CNT, or can wash with a solvent the composite film carried out the \*\* exception, and can control it to arbitration. And since a straight chain-like conjugated-system polymer has very high compatibility with CNT, even if a solvent washes several times, a straight chain-like conjugated-system polymer adheres 10% of the weight or more to CNT, and is binding between CNT. Thus, the obtained composite film can be made to bind firmly by sticking on the purpose part, or cutting after desiccation, imprinting with un-drying, and making it dry in the purpose part.

[0022] As a semi-conductor material, fields, such as a heat sink which used the high thermal conductivity of CNT for an antielectric ingredient, an electrode material, conductive coating material, etc. again, can also use the polymer composite of this invention as ingredients, such as a transistor, a solar battery, and a sensor, and a conductor material. Furthermore, although conductivity does not fall so much compared with the film which consists of a CNT simple substance, since fast higher \*\*\*\*\* can do homogeneity and a binding property, dependability of the composite film of this invention can improve and it can extend the application range as a conductor material.

[0023] In addition, in this invention, the electric conductivity of a polymer composite is the following, and is made and called for. That is, after forming one electrode in a glass substrate for metal layers (platinum, gold, etc.) by sputtering first, on this surface of metal, a composite polymer is used and a spinner is applied. Next, another electrode is formed in this spreading film front face by carrying out sputtering of the metal thin film. An electrical potential difference (V) is impressed to inter-electrode [ which sandwiches a polymer composite / above-mentioned / two ], the current at that time (I) is searched for, and electric conductivity is measured from a V-I property (2 terminal method). Moreover, a polymer composite is applied on the glass substrate with which 2 sets of Kushigata-like electrodes countered, and were formed, an electrical potential difference is impressed to inter-electrode [ 2 sets of ], and the method of asking for electric conductivity from the current at that time is also used. In addition, it can ask for electric conductivity from the 4 terminal method for having been 3 terminal method with a guard ring, when the electric conductivity of a composite polymer thin film was low, and having used four electrodes, when electric conductivity was high.

[0024] Moreover, in this invention, the mobility of a polymer composite is the following, and is made and called for. That is, after forming metal layers (platinum, gold, etc.) in a glass substrate by sputtering first, on this surface of metal, a composite polymer is used and a spinner is applied. Next, a metal thin film is formed in this spreading film front face by sputtering. The electrical potential difference (V) was impressed to inter-electrode [ which sandwiches a composite polymer ], and the current at that time (I) was searched for. A current (I) is degree type  $I = 9\epsilon\mu V^2/8d^3$  (1)

It is come out and expressed. If an electrical potential difference V is increased and it goes, I will go into the field of the space charge limited current proportional to the square of V from the OMIKKU behavior proportional to V.

[0025] In the above-mentioned formula (1), epsilon is [ mobility and d of the dielectric constant of a polymer composite and mu ] the thickness of the spreading film. Mobility mu is computed from a formula (1) in this field.

[0026]

[Example] Hereafter, this invention is explained still more concretely based on an example. However, this invention is not limited to the following example.

[0027] an example 1 -- first, 1g (monolayer carbon nanotube: the Science Laboratories make, 95% of purity) of CNT(s) was put in into the flask of 100mL, and it distributed [ chloroform 50mL ] for 1 hour using the ultrasonic washing machine. Next, 10g (the Aldrich make, molecular weight: Mw20000) of Polly 3-hexyl thiophenes was added as a straight chain-like conjugated-system polymer, and the ultrasonic washing machine distributed further for 10 hours. The obtained poly thiophene system polymer composite solution (10 % of the weight of ratios of CNT to a straight chain-like conjugated-system polymer) was taken out 0.3 mLs, it applied on the glass substrate with which 2 sets of Kushigata electrodes were formed, and the paint film was produced. The electric conductivity of this paint film was  $1.5 \times 10^{-1}$  S/cm from a V-I property.

[0028] On the other hand, in order to measure the electric conductivity of only a Polly 3-hexyl thiophene, the thin film of only a Polly 3-hexyl thiophene was obtained by dropping and carrying out the spin coat of the chloroform solution of only a Polly 3-hexyl thiophene on the glass substrate with which the disc electrode with 3 terminal method guard ring was formed. When the electric conductivity of this thin film was measured by 3 terminal method, it was abbreviation  $2 \times 10^{-9}$  S/cm. That is, improvement in the electric conductivity of about 8 figures was able to be aimed at by distribution of CNT.

[0029] Pori which is the polyphenylene vinylene (PPV) derivative used as a polymer of example of comparison 1 composite (composition of m-phenylenevinylene-co-2 and 5-dioctoxy-p-phenylenevinylene (henceforth PmPV) was performed by the well-known approach (109 Synthetic Metals, vol. 2478 (1999).) The 10-3 mol-concentration dissolution of the obtained PmPV was carried out into the toluene solvent, CNT was mixed 10% with the weight fraction to PmPV, and the composite solution was prepared. In addition, CNT used the same thing as an example 1. The supersonic wave was irradiated with the ultrasonic washing machine to this solution, and coating liquid was obtained. This coating liquid was applied on the glass substrate with which 2 sets of Kushigata electrodes were formed like the example 1, and the paint film was produced. When the electric conductivity of this paint film was measured like the example 1, it was  $1.8 \times 10^{-3}$  S/cm and was the electric conductivity of the abbreviation 1/100 of the composite obtained in the example 1. In addition, the electric conductivity only in PmPV was abbreviation  $1 \times 10^{-12}$  S/cm.

[0030] The composite polymer thin film was produced like the example 1 except having changed the amount of example 2CNT into 0.4g (4 % of the weight of weight ratios of CNT). When electric conductivity was measured using the Kushigata electrode like the example 1, it was  $2 \times 10^{-4}$  S/cm.

[0031] When the composite polymer thin film was produced like the example 1 of a comparison except having changed the weight ratio of CNT to example of comparison 2PmPV (molecular weight: Mw15000) to 4% of the weight and electric conductivity was measured using the Kushigata electrode like the example 1, electric conductivity was  $1 \times 10^{-10}$  S/cm.

[0032] The composite solution (the weight ratio of CNT: 0.7 % of the weight) was prepared like the example 1 except having changed the amount of example 3CNT into 0.07g. After irradiating a supersonic wave with an ultrasonic washing machine like an example 1 to this solution, it was left [ about ] on the 1st and the coating liquid for spinner spreading was obtained. On the glass substrate which produced the aluminum electrode 1 by vacuum evaporationo beforehand, this solution was applied and the film of about 1-micrometer thickness was formed. The voltage-current property of the spreading film was measured having formed the aluminum electrode 2 by vacuum evaporationo on this film furthermore, and impressing an electrical potential difference among the aluminum electrodes 1 and 2.

[0033] When it asked for mobility based on the formula (1) from the measurement result of this voltage-current property, it was  $6 \times 10^{-3} \text{ cm}^2/\text{V}\cdot\text{sec}$ .

[0034] On the other hand, when only the Polly 3-hexyl thiophene which does not contain CNT measured that by the same approach as the above, mobility was  $2 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{sec}$ . From this result, the improvement in one about 30 times the mobility of this was found by distribution of CNT.

[0035] The composite polymer thin film was produced like the example 1 except having changed the amount of example 4CNT into 2.5g (25 % of the weight of weight ratios of CNT to a straight chain-like conjugated-system polymer). It was 1.5 S/cm when electric conductivity was measured using the Kushigata electrode like the example 1.

[0036] The composite solution (the weight ratio of CNT to a straight-chain-like conjugated-system polymer: 50 % of the weight) was prepared like the example 1 except having changed the amount of chloroform into 5g for the amount of example 5CNT 500 mLs. this -- solution 5mL was diluted with chloroform to 100mL(s), and it carried out the \*\* exception using the membrane filter (ADVANTEC Co., Ltd. make) with 0.1 micrometers [ of apertures of PTFE ], and a diameter of 90mm. CNT which the straight chain-like conjugated-system polymer by which uptake was carried out bound on the filter was imprinted and dried on the glass substrate, and the composite film was obtained. When this composite film was firmly bound to the glass substrate and measured electric conductivity by 3 terminal method, it was 60S/cm. Moreover, when the CNT weight ratio was computed by elemental analysis, it was 110 % of the weight.

[0037] The composite solution prepared in the example 6 example 5 was diluted like the example 5, and it carried out the \*\* exception using the membrane filter, and it was made to dry and the film was obtained by removing from a filter. It was possible to have stuck on the part of arbitration firmly by being able to cut this composite film into the size of arbitration, making the chloroform of a minute amount swell it, and making it dry.

[0038] The composite solution prepared in the example 7 example 5 was diluted like the example 5, and it carried out the \*\* exception using the membrane filter, and CNT bound with the straight chain-like conjugated-system polymer which carried out uptake on the filter was again dissolved in chloroform 500mL, these dispersion liquid were distributed for 10 minutes with the ultrasonic washing machine, and it carried out the \*\* exception with the same filter. CNT bound with the straight chain-like conjugated-system polymer by which uptake was carried out on the filter was imprinted and dried on the glass substrate, and the film of CNT bound with the straight chain-like conjugated-system polymer was obtained. When this composite film was firmly bound to the glass substrate and measured electric conductivity by 3 terminal method, it was 95S/cm. Moreover,

when the CNT weight ratio was computed by elemental analysis, it was 900 % of the weight.

[0039] By the same approach as example 8 example 7, the composite solution was processed, on the filter, uptake of the CNT bound with the straight chain-like conjugated-system polymer is carried out, it was dried, and the composite film was obtained by removing from a filter. It was possible to have stuck on the part of arbitration firmly by being able to cut this composite film into the size of arbitration, making the chloroform of a minute amount swell it, and making it dry.

[0040] 1g of CNT(s) was put in into the flask of example of comparison 3100mL, and it distributed [ chloroform 50mL ] for 1 hour using the ultrasonic washing machine.

Furthermore this dispersion-liquid 5mL was isolated preparatively, and it diluted to 100mL(s), and distributed for 1 hour using the ultrasonic washing machine further. Although a part of CNT had been condensed, it imprinted and dried CNT by which carried out CNT the \*\* exception on the filter like the example 5, and uptake was carried out on the filter on the glass substrate, and obtained the CNT film. Although it was  $1.2 \times 10^1$  S/cm when electric conductivity was measured by 3 terminal method, this CNT film had the very small binding capacity to a glass substrate, and CNT was separating extent in light friction.

[0041]

[Effect of the Invention] Since it is what consists of a monolayer carbon nanotube or a multilayer carbon nanotube, and a straight chain-like conjugated-system polymer, the polymer composite of this invention is excellent in the dispersibility of a carbon nanotube, is adjusting the amount of a carbon nanotube and can be used as a material which was excellent as a semi-conductor material and a conductor material.

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**TECHNICAL FIELD**

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**[Field of the Invention]** This invention relates to the polymer composite which consists of a carbon nanotube and a straight chain-like conjugated-system polymer.

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PRIOR ART

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[Description of the Prior Art] Applied possibility is examined by the extensive field as a material with nanotechnology leading [ a carbon nanotube (henceforth CNT) ]. It is divided into the approach of using the single track of CNT like a transistor or the probe for microscopes as an application, and the approach of summarizing much CNT(s) like an electron emission electrode, the electrode for fuel cells, or the conductive composite that distributed CNT, and using it as bulk. Although it is indispensable that it can distribute good in the polymer which serves as a matrix material in a conductive composite etc., generally CNT has the problem of being hard to distribute. For this reason, the approach of improving dispersibility by reforming on the front face of CNT, chemical modification, etc. is taken.

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**EFFECT OF THE INVENTION**

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**[Effect of the Invention]** Since it is what consists of a monolayer carbon nanotube or a multilayer carbon nanotube, and a straight chain-like conjugated-system polymer, the polymer composite of this invention is excellent in the dispersibility of a carbon nanotube, is adjusting the amount of a carbon nanotube and can be used as a material which was excellent as a semi-conductor material and a conductor material.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, when the front face of CNT is reformed, there is a problem that the property of original CNT, for example, high conductivity, is spoiled. As an approach of making a polymer distributing CNT, the method of making a spiral polymer distribute CNT is learned, without reforming the front face of CNT. As such a polymer, Poly m-phenylenevinylene-co-dioctoxy-p-phenylenevinylene (patent reference 1 reference), a polyvinyl pyrrolidone (nonpatent literature 1 reference), and Poly-phenylacetylene are used, for example. However, since conjugated system will not be enough connected if spiral structure is generally taken, a motion of the charge within a polymer is late and there is a trouble of being inadequate for using conductivity and a semi-conductor property.

[0004] Then, that this invention should solve the above-mentioned trouble, it excels in the dispersibility of CNT and sets it as the purpose to offer the polymer composite which can control electric conductivity by concentration of CNT.

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## MEANS

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[Means for Solving the Problem] In order to attain the above-mentioned technical problem, this invention consists of the following configuration.

[0008] That is, this invention is a polymer composite which consists of a monolayer carbon nanotube or a multilayer carbon nanotube, and a straight chain-like conjugated-system polymer.

[0009]

[Embodiment of the Invention] As a result of considering distribution of CNT to a polymer wholeheartedly that the polymer composite which consists of CNT and a polymer should be developed, even if this invention persons were polymers which do not take spiral structure, they found out that it could distribute good. Furthermore, the polymer used in this invention has the features of being advantageous to conjugated-system structure being developed and using conductivity and a semi-conductor property in order not to take spiral structure.

[0010] Generally, a conjugated-system macromolecule can control conductivity by doping from a semiconductor region to a metal field, and things are known. Doping is performed by adding to a conjugated-system macromolecule by making electronic receptiveness or an electron-donative organic compound into a dopant. However, generally the doped conjugated-system macromolecule lacks in stability to heat or humidity, and when exposed to an elevated temperature or high humidity, it has the trouble that electric conductivity decreases greatly. This is for a dopant to secede from a conjugated-system macromolecule mainly under such conditions. In the polymer composite which consists of CNT and the polymer of this invention, electric conductivity can be controlled by concentration of CNT, and there are the features that the stability over heat or humidity is also excellent.

[0011] Hereafter, this invention is explained in full detail. The polymer which constitutes a composite in this invention needs to be a straight chain-like conjugated-system polymer. The skeletal structure of a macromolecule does not take spiral structure in a stable state (condition that external force is not added), the shape of a straight chain means a straight stretch \*\*\*\*\* thing, and, as for a conjugated-system polymer, association of the carbon-carbon of a macromolecule frame means the polymer with which 1-fold association and double association stand in a row by turns here.

[0012] As such a conjugated-system polymer, the poly thiophene system polymer, a polypyrrole system polymer, the poly aniline system polymer, a polyacetylene system polymer, a Polly p-phenylene system polymer, a Polly p-phenylenevinylene system polymer, etc. are mentioned. In order for these conjugated-system polymers to be straight chains-like, as for the poly thiophene system polymer and a polypyrrole system polymer,

a monomeric unit needs to be connected in the 2 or 5th place of a thiophene ring and a pyrrole ring, respectively. Moreover, with the Polly p-phenylene system polymer and the Polly p-phenylenevinylene system polymer, the macromolecule frame is connected in the para position of a phenylene group. In this invention, the poly thiophene system polymer is especially used preferably also in the above-mentioned polymer.

[0013] The poly thiophene system polymer has the structure to which the side chain was attached to the polymer with the frame of Polly p-thiophene structure. As an example, Polly 3-methylthiophene, a Polly 3-butyl thiophene, Polly 3-alkyl thiophenes, such as a Polly 3-hexyl thiophene, a Polly 3-octyl thiophene, and a Polly 3-DESHIRU thiophene (especially for a limit, the carbon number of an alkyl group is 1-12 preferably, although there is nothing), Polly 3-alkoxy thiophenes, such as a Polly 3-methoxy thiophene, a Polly 3-ethoxy thiophene, and a Polly 3-dodecyloxy thiophene (especially for a limit, the carbon number of an alkoxy group is 1-12 preferably, although there is nothing), Polly 3-alkoxy-4-alkyl thiophenes (especially for a limit, the carbon number of an alkoxy group and an alkyl group is 1-12 preferably, although there is nothing), such as Polly 3-methoxy-4-methylthiophene and Polly 3-dodecyloxy-4-methylthiophene, are mentioned. One sort or two sorts or more can be used. Especially, a Polly 3-alkyl thiophene and a Polly 3-alkoxy thiophene are desirable, and a Polly 3-hexyl thiophene is desirable especially as the former. Moreover, the above-mentioned polymer does not necessarily need to be the amount of macromolecules, and may be oligomer which consists of straight chain-like conjugated system.

[0014] Although CNT is produced by the arc discharge method, the chemical-vapor-deposition method (it considers as a CVD method below), the laser ablation method, etc., CNT used for this invention may be obtained by which approach. Moreover, there are a monolayer carbon nanotube (henceforth SWCNT) around which the carbon film (GURAFFEN sheet) of one sheet was wound in the shape of a cylinder, and a multilayer carbon nanotube (henceforth MWCNT) with which two or more GURAFFEN sheets of two or more sheets were wound around concentric circular in CNT, in this invention, it is a simple substance about SWCNT and MWCNT, respectively, or both sides are used for coincidence. Especially SWCNT is preferably used at the point which raises the mobility of a polymer composite and raises a semi-conductor property.

[0015] Since fullerene, graphite, and amorphous carbon are generated by coincidence as a byproduct and catalyst metals, such as nickel, iron, cobalt, and an yttrium, also remain in case SWCNT and MWCNT are produced by the above-mentioned approach, it is necessary to refine these impurities. Moreover, although CNT is generally formed in the shape of a string, when it is the conductive low range or uses a composite as a semi-conductor, it is desirable to cut CNT, before using a staple fiber-like thing or a fibrous thing. Sonication is effective in purification of the above-mentioned impurity or the cut to a staple fiber with the acid treatment by the nitric acid, a sulfuric acid, etc., and it is still more desirable to use separation with a filter together, when raising purity.

Although especially the diameter of CNT used by this invention is not limited, 1nm or more 100nm or less is desirable, and is 50nm or less more preferably.

[0016] It is obtained in the configuration which carried out orientation to the substrate front face perpendicularly by forming catalyst metals, such as iron and cobalt, for example on a substrate, pyrolyzing a carbon compound at 700-900 degrees C with a CVD method on the front face, and carrying out vapor growth of the CNT as an approach of

producing CNT in the shape of a staple fiber beforehand. Thus, the produced shape of a staple fiber CNT can be taken out by stripping off from a substrate etc. Moreover, the shape of a staple fiber CNT can make a catalyst metal able to support on a porous base material like porous silicon, and the oxide film on anode of an alumina, and can also grow up CNT into the front face with a CVD method. CNT of the shape of a staple fiber which used as the raw material a molecule like the iron phthalocyanine which contains a catalyst metal in intramolecular, and carried out orientation also by the approach of producing CNT on a substrate by performing a CVD method in the gas stream of an argon/hydrogen is producible. Furthermore, the shape of a staple fiber CNT which carried out orientation to the SiC single crystal front face with the epitaxial grown method can also be acquired.

[0017] In this invention, by mixing the thing which made the straight chain-like conjugated-system polymer distribute CNT in a suitable solvent, a composite solution can be prepared and the polymer composite of this invention can be obtained from this composite solution.

[0018] As a solvent used here, straight chain-like conjugated-system polymers, such as a methanol, toluene, a xylene, and chloroform, can mention a meltable thing preferably. Thus, with an ultrasonic washing machine, after irradiating a supersonic wave preferably for about 20 hours for several hours, in the obtained solution, it will be left about one day, and the coating liquid for spinner spreading can be obtained in it.

[0019] The above-mentioned conjugated-system polymer not only distributes CNT good, but is equipped with the features of making it distribute, while solving CNT condensed [ especially ] in the shape of a bundle by SWCNT in the state of the solution. Generally it is desirable that are condensing SWCNT in the shape of a bundle in the condition of having been manufactured, and CNT is solved and distributed from this bundle condition in a composite. For this reason, it is used, after giving chemical modification by the approach of making a functional group add to SWCNT etc. and giving dispersibility, as seen also in Science magazine vol.282 and p95 (1998) when SWCNT is distributed. However, since pi conjugated system which constitutes CNT will be easy to be destroyed if chemical modification is given to CNT, there is a trouble that the property of CNT original is spoiled. Distribution of CNT is possible even if it does not give such chemical modification especially in this invention.

[0020] Although especially the weight ratio of CNT contained in the polymer composite of this invention is not limited, when the molar fraction of CNT exceeds 3 % of the weight, for example to a straight chain-like conjugated-system polymer, conductivity can be raised by leaps and bounds. At 3 or less % of the weight, although the molar fraction of CNT cannot make conductivity increase greatly, it can give the conductivity of extent which misses electrostatic charge. The mobility of a charge when the weight ratio of CNT uses a polymer composite as a semi-conductor material 0.1% of the weight or more to a straight chain-like conjugated-system polymer especially as it is 1 or less % of the weight can be raised, and it can use as a high performance semi-conductor material, and is desirable. On the other hand, since the conductivity of a polymer composite can be raised by leaps and bounds if the weight ratio of CNT increases, it can use as a conductor ingredient. Especially the weight ratio of CNT can exceed 3 % of the weight, and it can treat as a conductor ingredient to 900 or less % of the weight of a case. Furthermore, when the weight ratios of CNT are 100 % of the weight or more and 900 % of the weight

or less, a matrix serves as CNT and the conductor composite of a gestalt to which a polymer exists in the clearance between CNT(s) can be obtained. Since this composite can be fabricated in the shape of a film, a composite film can be obtained, and since it can balance highly, the reinforcement as a film, conductivity, and binding capacity can be used preferably.

[0021] As an approach of obtaining a film-like composite, it consists of a straight chain-like conjugated-system polymer, CNT, and a solvent, and can obtain from the CNT distribution solution whose weight ratios of CNT to a straight chain-like conjugated-system polymer are 3 % of the weight or more and 900 % of the weight or less by classifying CNT which the straight chain-like conjugated-system polymer bound, for example. Although a filter is used, a distributed solution is carried out a \*\* exception or there is a method of it evaporating or being air-dry and classifying a solvent from a distributed solution etc. among the judgment approaches, when especially a \*\* exception is performed, the weight ratio of CNT to a straight chain-like conjugated-system polymer can obtain 100% of the weight or more of a composite film. In addition, the ratio of the CNT and the straight chain-like conjugated-system polymer in a composite film is computable from the ratio of the carbon by elemental analysis, hydrogen, nitrogen, and sulfur. Moreover, this ratio can change the compounding ratio of the straight chain-like conjugated-system polymer in CNT dispersion liquid, and CNT, or can wash with a solvent the composite film carried out the \*\* exception, and can control it to arbitration. And since a straight chain-like conjugated-system polymer has very high compatibility with CNT, even if a solvent washes several times, a straight chain-like conjugated-system polymer adheres 10% of the weight or more to CNT, and is binding between CNT. Thus, the obtained composite film can be made to bind firmly by sticking on the purpose part, or cutting after desiccation, imprinting with un-drying, and making it dry in the purpose part.

[0022] As a semi-conductor material, fields, such as a heat sink which used the high thermal conductivity of CNT for an antielectric ingredient, an electrode material, conductive coating material, etc. again, can also use the polymer composite of this invention as ingredients, such as a transistor, a solar battery, and a sensor, and a conductor material. Furthermore, although conductivity does not fall so much compared with the film which consists of a CNT simple substance, since fast higher \*\*\*\*\* can do homogeneity and a binding property, dependability of the composite film of this invention can improve and it can extend the application range as a conductor material.

[0023] In addition, in this invention, the electric conductivity of a polymer composite is the following, and is made and called for. That is, after forming one electrode in a glass substrate for metal layers (platinum, gold, etc.) by sputtering first, on this surface of metal, a composite polymer is used and a spinner is applied. Next, another electrode is formed in this spreading film front face by carrying out sputtering of the metal thin film. An electrical potential difference (V) is impressed to inter-electrode [ which sandwiches a polymer composite / above-mentioned / two ], the current at that time (I) is searched for, and electric conductivity is measured from a V-I property (2 terminal method). Moreover, a polymer composite is applied on the glass substrate with which 2 sets of Kushigata-like electrodes countered, and were formed, an electrical potential difference is impressed to inter-electrode [ 2 sets of ], and the method of asking for electric conductivity from the current at that time is also used. In addition, it can ask for electric conductivity from the 4

terminal method for having been 3 terminal method with a guard ring, when the electric conductivity of a composite polymer thin film was low, and having used four electrodes, when electric conductivity was high.

[0024] Moreover, in this invention, the mobility of a polymer composite is the following, and is made and called for. That is, after forming metal layers (platinum, gold, etc.) in a glass substrate by sputtering first, on this surface of metal, a composite polymer is used and a spinner is applied. Next, a metal thin film is formed in this spreading film front face by sputtering. The electrical potential difference (V) was impressed to inter-electrode [ which sandwiches a composite polymer ], and the current at that time (I) was searched for. A current (I) is degree type  $I = 9\epsilon\mu V^2/8d^3$  (1)

It is come out and expressed. If an electrical potential difference V is increased and it goes, I will go into the field of the space charge limited current proportional to the square of V from the OMIKKU behavior proportional to V.

[0025] In the above-mentioned formula (1), epsilon is [ mobility and d of the dielectric constant of a polymer composite and mu ] the thickness of the spreading film. Mobility mu is computed from a formula (1) in this field.

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[Translation done.]

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EXAMPLE

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[Example] Hereafter, this invention is explained still more concretely based on an example. However, this invention is not limited to the following example.

[0027] an example 1 -- first, 1g (monolayer carbon nanotube: the Science Laboratories make, 95% of purity) of CNT(s) was put in into the flask of 100mL, and it distributed [ chloroform 50mL ] for 1 hour using the ultrasonic washing machine. Next, 10g (the Aldrich make, molecular weight: Mw20000) of Polly 3-hexyl thiophenes was added as a straight chain-like conjugated-system polymer, and the ultrasonic washing machine distributed further for 10 hours. The obtained poly thiophene system polymer composite solution (10 % of the weight of ratios of CNT to a straight chain-like conjugated-system polymer) was taken out 0.3 mLs, it applied on the glass substrate with which 2 sets of Kushigata electrodes were formed, and the paint film was produced. The electric conductivity of this paint film was  $1.5 \times 10^{-1}$  S/cm from a V-I property.

[0028] On the other hand, in order to measure the electric conductivity of only a Polly 3-hexyl thiophene, the thin film of only a Polly 3-hexyl thiophene was obtained by dropping and carrying out the spin coat of the chloroform solution of only a Polly 3-hexyl thiophene on the glass substrate with which the disc electrode with 3 terminal method guard ring was formed. When the electric conductivity of this thin film was measured by 3 terminal method, it was abbreviation  $2 \times 10^{-9}$  S/cm. That is, improvement in the electric conductivity of about 8 figures was able to be aimed at by distribution of CNT.

[0029] Pori which is the polyphenylene vinylene (PPV) derivative used as a polymer of example of comparison 1 composite (composition of m-phenylenevinylene-co-2 and 5-dioctoxy-p-phenylenevinylene (henceforth PmPV) was performed by the well-known approach (109 Synthetic Metals, vol. 2478 (1999)).) The 10-3 mol-concentration dissolution of the obtained PmPV was carried out into the toluene solvent, CNT was mixed 10% with the weight fraction to PmPV, and the composite solution was prepared. In addition, CNT used the same thing as an example 1. The supersonic wave was irradiated with the ultrasonic washing machine to this solution, and coating liquid was obtained. This coating liquid was applied on the glass substrate with which 2 sets of Kushigata electrodes were formed like the example 1, and the paint film was produced. When the electric conductivity of this paint film was measured like the example 1, it was  $1.8 \times 10^{-3}$  S/cm and was the electric conductivity of the abbreviation 1/100 of the composite obtained in the example 1. In addition, the electric conductivity only in PmPV was abbreviation  $1 \times 10^{-12}$  S/cm.

[0030] The composite polymer thin film was produced like the example 1 except having changed the amount of example 2CNT into 0.4g (4 % of the weight of weight ratios of CNT). When electric conductivity was measured using the Kushigata electrode like the

example 1, it was  $2 \times 10^{-4}$  S/cm.

[0031] When the composite polymer thin film was produced like the example 1 of a comparison except having changed the weight ratio of CNT to example of comparison 2PmPV (molecular weight: Mw15000) to 4% of the weight and electric conductivity was measured using the Kushigata electrode like the example 1, electric conductivity was  $1 \times 10^{-10}$  S/cm.

[0032] The composite solution (the weight ratio of CNT: 0.7 % of the weight) was prepared like the example 1 except having changed the amount of example 3CNT into 0.07g. After irradiating a supersonic wave with an ultrasonic washing machine like an example 1 to this solution, it was left [ about ] on the 1st and the coating liquid for spinner spreading was obtained. On the glass substrate which produced the aluminum electrode 1 by vacuum evaporationo beforehand, this solution was applied and the film of about 1-micrometer thickness was formed. The voltage-current property of the spreading film was measured having formed the aluminum electrode 2 by vacuum evaporationo on this film furthermore, and impressing an electrical potential difference among the aluminum electrodes 1 and 2.

[0033] When it asked for mobility based on the formula (1) from the measurement result of this voltage-current property, it was  $6 \times 10^{-3}$  cm<sup>2</sup>/V·sec.

[0034] On the other hand, when only the Polly 3-hexyl thiophene which does not contain CNT measured that by the same approach as the above, mobility was  $2 \times 10^{-4}$  cm<sup>2</sup>/V·sec. From this result, the improvement in one about 30 times the mobility of this was found by distribution of CNT.

[0035] The composite polymer thin film was produced like the example 1 except having changed the amount of example 4CNT into 2.5g (25 % of the weight of weight ratios of CNT to a straight chain-like conjugated-system polymer). It was 1.5 S/cm when electric conductivity was measured using the Kushigata electrode like the example 1.

[0036] The composite solution (the weight ratio of CNT to a straight-chain-like conjugated-system polymer: 50 % of the weight) was prepared like the example 1 except having changed the amount of chloroform into 5g for the amount of example 5CNT 500 mLs. this -- solution 5mL was diluted with chloroform to 100mL(s), and it carried out the \*\* exception using the membrane filter (ADVANTEC Co., Ltd. make) with 0.1 micrometers [ of apertures of PTFE ], and a diameter of 90mm. CNT which the straight chain-like conjugated-system polymer by which uptake was carried out bound on the filter was imprinted and dried on the glass substrate, and the composite film was obtained. When this composite film was firmly bound to the glass substrate and measured electric conductivity by 3 terminal method, it was 60S/cm. Moreover, when the CNT weight ratio was computed by elemental analysis, it was 110 % of the weight.

[0037] The composite solution prepared in the example 6 example 5 was diluted like the example 5, and it carried out the \*\* exception using the membrane filter, and it was made to dry and the film was obtained by removing from a filter. It was possible to have stuck on the part of arbitration firmly by being able to cut this composite film into the size of arbitration, making the chloroform of a minute amount swell it, and making it dry.

[0038] The composite solution prepared in the example 7 example 5 was diluted like the example 5, and it carried out the \*\* exception using the membrane filter, and CNT bound with the straight chain-like conjugated-system polymer which carried out uptake on the filter was again dissolved in chloroform 500mL, these dispersion liquid were distributed

for 10 minutes with the ultrasonic washing machine, and it carried out the \*\* exception with the same filter. CNT bound with the straight chain-like conjugated-system polymer by which uptake was carried out on the filter was imprinted and dried on the glass substrate, and the film of CNT bound with the straight chain-like conjugated-system polymer was obtained. When this composite film was firmly bound to the glass substrate and measured electric conductivity by 3 terminal method, it was 95S/cm. Moreover, when the CNT weight ratio was computed by elemental analysis, it was 900 % of the weight.

[0039] By the same approach as example 8 example 7, the composite solution was processed, on the filter, uptake of the CNT bound with the straight chain-like conjugated-system polymer is carried out, it was dried, and the composite film was obtained by removing from a filter. It was possible to have stuck on the part of arbitration firmly by being able to cut this composite film into the size of arbitration, making the chloroform of a minute amount swell it, and making it dry.

[0040] 1g of CNT(s) was put in into the flask of example of comparison 3100mL, and it distributed [ chloroform 50mL ] for 1 hour using the ultrasonic washing machine. Furthermore this dispersion-liquid 5mL was isolated preparatively, and it diluted to 100mL(s), and distributed for 1 hour using the ultrasonic washing machine further. Although a part of CNT had been condensed, it imprinted and dried CNT by which carried out CNT the \*\* exception on the filter like the example 5, and uptake was carried out on the filter on the glass substrate, and obtained the CNT film. Although it was  $1.2 \times 10^1$  S/cm when electric conductivity was measured by 3 terminal method, this CNT film had the very small binding capacity to a glass substrate, and CNT was separating extent in light friction.

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[Translation done.]